Supporting Information for

Regulating piezofluorochromism of 9,10-bis(butoxystyryl)anthracenes by isomerization of butyl group

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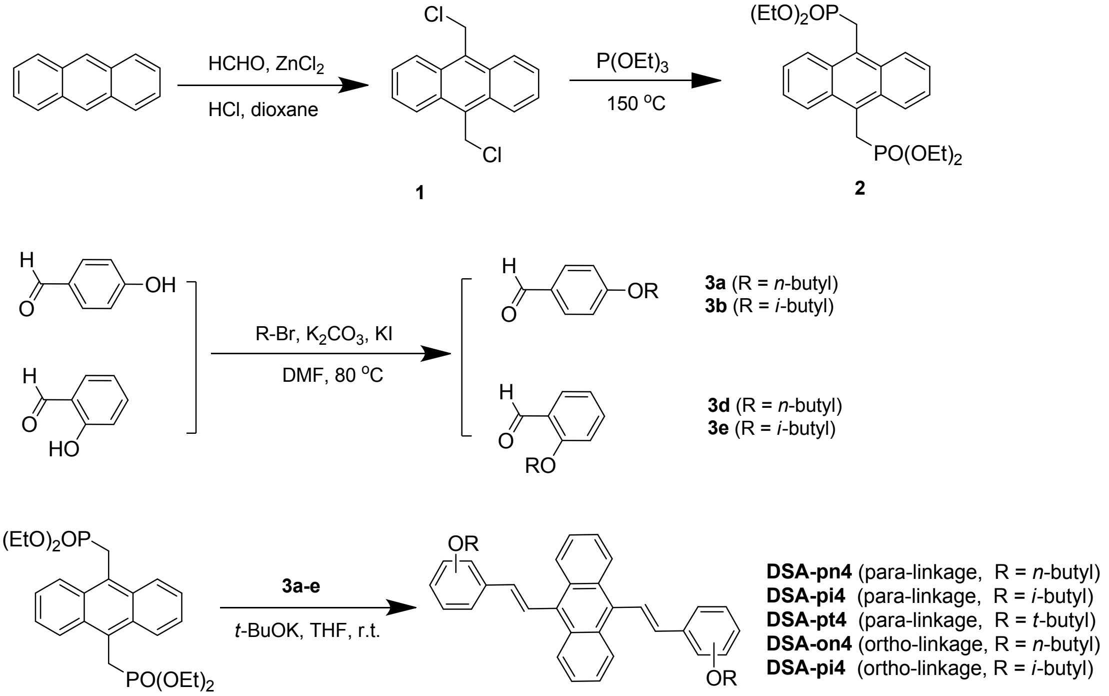
Contents

1 Experimental section

Materials and measurements

Anthracene, paraformaldehyde, 2-hydroxybenzaldehyde, *n*-butyl bromide, 4-hydroxybenzaldehyde, *i*-butyl bromide and *t*-butyl bromide were purchased from Tianjin Guangfu Fine Chemical Reagents Company (China) and used as received. Other common reagents and solvents were purchased as analytical grade from Tianjin Jiangtian Chemical technology Co., LTD (China) and used without further purification. Tetrahydrofuran (THF) was distilled from sodium/benzophenone before use. Deionized water was employed throughout this study. 9,10-Bis(chloromethyl) anthracene[1] (**1**), 9,10-bis(diethylphosphorylmethyl)anthracene [2] (**2**) and butoxy substituted benzaldehydes[3] (**3a, 3b, 3d** and **3e**) were prepared according to the literature methods. 4-(*t*-Butoxy)benzaldehyde (**3c**) was purchased as analytical grade from Tokyo Chemical Industry Co., LTD. Isomers of **DSA_4**, including *n*-butyl, *i*-butyl and *t*-butyl at *ortho* or *para* positions were successfully synthesized by Wittig–Horner reactions of corresponding butoxy substituted benzaldehydes and 9,10-bis(diethoxyphosphorylmethyl)anthracene[4], described in **Scheme 1.**

NMR spectra were measured on a Bruker AVANCE III spectrometer (600 MHz for ^{1}H NMR and 150 MHz for ^{13}C NMR) with $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard. High-resolution mass spectra (HRMS) were measured with a Bruker Daltonics micrOTOF-Q II instrument. Photoluminescence spectra (PL) were measured on a Hitachi F-4500 spectrometer with a slit width of 1.5 nm for both excitation and emission. TGA (thermal gravimetric analysis) was measured on an STA 409PC with a heating rate of 10 °C /min from room temperature to 800 °C in a stream of N_2 (40 mL/min). High Performance Liquid Chromatography was conducted on a Baker Norton pharmaceuticals detector with a baseline C_{18}-column at 365 nm under 1 mL/min of mobile phase by gradient elution with the ratio (V:V) of methylene chloride and methanol from 20:80 to 30:70, data was collected and analyzed with the N2000 chromatography data system. Differential scanning calorimetry (DSC) curves were obtained with a Perkin Elmer Diamond DSC at heating rates of 10 °C/min under N_2 atmosphere. Wide-angle X-ray diffraction (WAXD) measurements were performed by using a Rigaku X-ray diffractometer (D/MAX-2500) at a scanning rate of 4°/min. THF aqueous solution of certain concentration was made up by addition of water into the THF solutions of samples under vigorous stirring at room temperature. The concentrations of all samples were adjusted to 1.0×10^{-5} μM by adding water. Grinding experiment: filter paper was soaked in the solution of pristine solid and then ground with a metal spatula at room temperature. Pressing experiment: pristine solid and KBr powder (w/w, 1:50) was simply mixed in a mortar and then pressed with IR pellet press for 1 min at room temperature under the pressure of 1500 psi. Solvent-fuming experiment: The ground sample was exposed to the dichloromethane vapor for 1 min at room temperature.



Scheme 1 Synthesis and structures of DSA_4

9,10-Bis(chloromethyl)anthracene (1)

To a mixture of anthracene (8.90 g, 50 mmol) and paraformaldehyde (7.50 g, 250 mmol) in dioxane (100 mL) was dropwise added concentrated hydrochloric acid (200 mL) at room temperature under N_2 atmosphere. Then the solution was heated and slowly stirred under gentle reflux for 3 h. After this, the reaction mixture was allowed to stand for 16 h. The crude product was obtained by filtration and washed with 1,4-dioxane and water until pH = 7. Finally，its recrystallization in toluene yields a yellow solid (8.44g, 60% yield). ^{1}H NMR (600MHz, $CDCl_3$, ppm): 8.40-8.38 (m, 4H), 7.67-7.66 (m, 4H), 5.61(s, 4H).

9,10-Bis(diethylphosphorylmethyl)anthracene (2)

A solution of compound **1** (7.80 g, 28 mmol) and triethyl phosphate (30 ml) was stirred vigorously at gentle reflux for 12 h. After cooling down to room temperature, it was purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1/1, v/v) to give 8.16 g of compound **2** as a yellow solid (59% yield). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 8.38-8.37 (m, 4H), 7.58-7.56 (m, 4H), 4.21 (d, 4H, J = 19.8 Hz), 3.91-3.86 (m, 4H), 3.82-3.78(m, 4H), 1.06 (t, 12H, J = 7.2 Hz).

4-(*n*-Butoxy)benzaldehyde (3a)

To a solution of 4-hydroxybenzaldehyde (3.00 g, 24 mmol) in dry DMF (30 mL), K_2CO_3 (3.18 g, 30 mmol) and KI (catalytic amount) were added. The mixture was stirred and heated to 80 °C, followed by slow addition of *n*-butyl bromide (2.4 ml, 27 mmol). The mixture was continually stirred for 8 h at this temperature. After cooling to room temperature, it was poured into brine (50 mL) and extracted with dichloromethane (3×30 mL). The organic phases were combined, dried over $MgSO_4$ and concentrated to afford a brownish liquid (3.30 g, 65 %).

4-(*i*-Butoxy)benzaldehyde (**3b**), 2-(*n*-butoxy)benzaldehyde (**3d**) and 2-(*i*-butoxy)benzaldehyde (**3e**) were synthesized by the same method. **9,10-Bis(4-(*n*-butoxy)styryl)anthracenes (DSA-pn4)**

To the solution of compounds **2** (0.60 g, 1.26 mmol) and **3a** (0.40 g, 2.76 mmol) dissolved in 40 mL of dry THF, potassium *t*-butoxide (0.30 g, 2.76 mmol) was added. The obtained suspension was stirred at room temperature for 8 h. After removing the solvent under reduced pressure, the residue was recrystallized in THF/MeOH (1/10, v/v). The yellow solids were collected by filtration, washed with methanol, then purified by flash chromatography (petroleum ether/methylene chloride, 5/1, v/v) to afford 0.43 g **DSA-pn4** as a yellow-green solid in 76 % yield. m.p. 214-215 °C. ^{1}H NMR (600MHz, CDCl$_3$) δ (ppm): 8.41-8.40 (m, 4H), 7.78 (d, 2H, J = 16.2 Hz), 7.62 (d, 4H, J = 8.4 Hz), 7.47-7.45 (m,4H), 6.99 (d, 4H, J = 8.4 Hz), 6.88 (d, 2H, J = 16.2 Hz), 4.05 (t, 4H, J = 6.6 Hz), 1.85-1.80 (m, 4H), 1.56-1.54 (m, 4H), 1.02 (t, 6H, J = 6.6 Hz); ^{13}C NMR (150MHz, CDCl$_3$) δ (ppm): 159.34, 137.04, 132.94, 130.16, 129.78, 127.91, 126.68, 125.21, 122.90, 114.98, 68.00, 31.48, 19.42, 14.03. HRMS (ESI): calcd. for $C_{38}H_{38}O_2H$ 527.2945 [M + H]$^+$; found 527.2944. Purity: 96.95% (HPLC, t_R = 10.607 min).

DSA-pi4, **DSA-pt4**, **DSA-on4** and **DSA-oi4** were obtained by the same procedure.

DSA-pi4: Yield 78%, m.p. 201-203 °C. ^{1}H NMR (600MHz, CDCl$_3$) δ (ppm): 8.41-8.40 (m, 4H), 7.78 (d, 2H, J = 16.8 Hz), 7.62 (d, 4H, J = 8.4 Hz), 7.47-7.45 (m, 4H), 6.99 (d, 4H, J = 8.4 Hz), 6.88 (d, 2H, J = 16.8 Hz), 3.81 (d, 4H, J = 6.6 Hz), 2.17-2.12 (m, 2H), 1.07 (d, 12H, J = 6.6 Hz); ^{13}C NMR (150MHz, CDCl$_3$) δ (ppm): 159.49, 137.07, 132.96, 130.15, 129.80, 127.91, 126.69, 125.22, 122.90, 115.03, 74.76, 29.85, 28.46, 19.44. HRMS (ESI): calcd. for $C_{38}H_{38}O_2H$ 527.2945 [M + H]$^+$; found 527.2945. Purity: 99.30% (HPLC, t_R = 9.373 min).

DSA-pt4: Yield 90%, m.p. 216-218 °C. ^{1}H NMR (600MHz, CDCl$_3$) δ(ppm): 8.42-8.41 (m, 4H), 7.83 (d, 2H, J = 16.8 Hz), 7.61 (d, 4H, J = 8.4 Hz), 7.48-7.46 (m, 4H), 7.11 (d, 4H, J = 8.4 Hz), 6.91 (d, 2H, J = 16.8 Hz), 1.44 (s, 18H); ^{13}C NMR (150MHz, CDCl$_3$) δ (ppm): 155.65, 137.06, 132.89, 132.71, 129.75, 126.67, 125.29, 124.55, 123.99, 76, 95, 29.07. HRMS (ESI): calcd. for $C_{38}H_{38}O_2H$ 527.2945 [M + H]$^+$; found 527.2945. Purity: 98.33% (HPLC, t_R = 12.665 min).

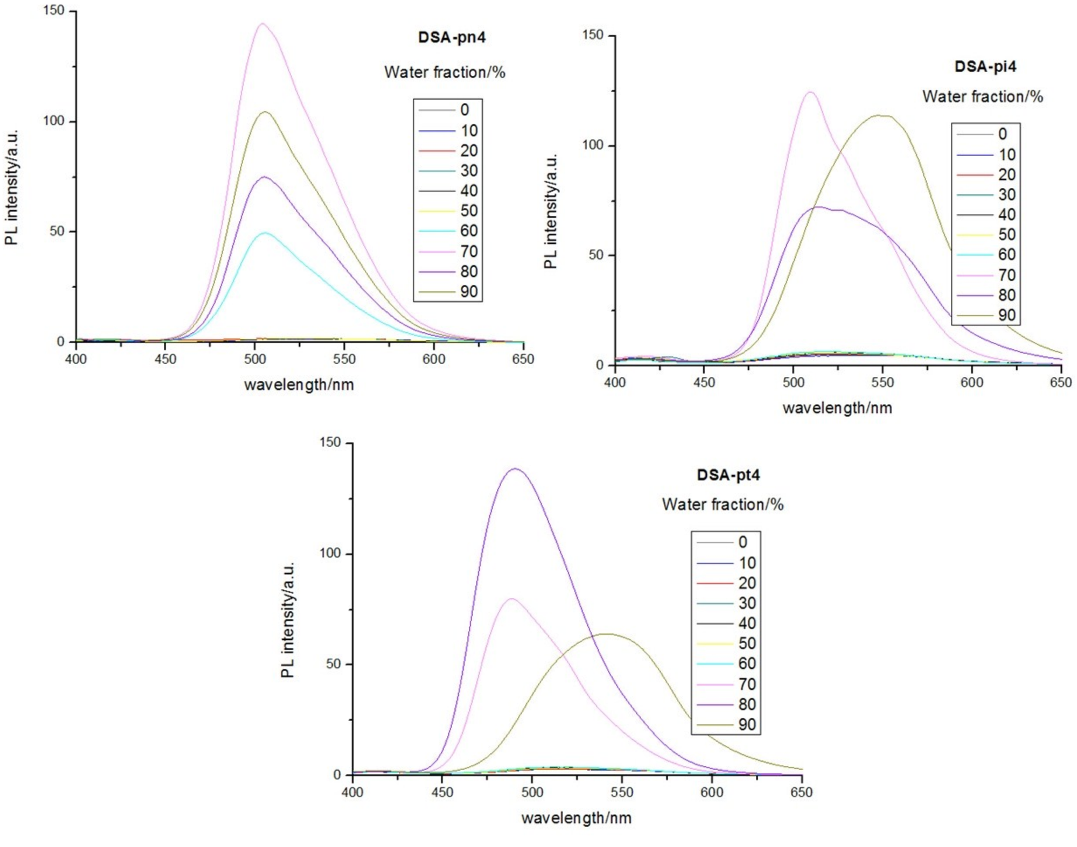
DSA-on4: Yield 81%, m.p. 174-175 °C. ^{1}H NMR (600MHz, CDCl$_3$) δ(ppm): 8.51-8.49 (m, 4H), 7.98 (d, 2H, J = 16.8 Hz), 7.83(d, 2H, J = 7.8 Hz), 7.50-7.49 (m, 4H), 7.31 (d, 4H, J = 16.8 Hz), 7.09 (t, 2H, J = 7.2 Hz), 7.00 (d, 2H, J = 7.8 Hz), 4.08 (t, 4H, J = 6.6 Hz), 1.83-1.78 (m, 4H), 1.54-1.49 (m, 4H), 0.95 (t, 6H, J = 6.6 Hz); ^{13}C NMR (150MHz, CDCl$_3$) δ (ppm): 156.92, 133.49, 133.11, 129.73, 129.05, 127.36, 126.80, 125.96, 125.17, 120.76, 112.14, 68.18, 31.57, 19.54, 13.98. HRMS (ESI): calcd. for $C_{38}H_{38}O_2H$ 527.2945 [M + H]$^+$; found 527.2946. Purity: 97.40% (HPLC, t_R = 12.298 min).

DSA-oi4: Yield 80%, m.p. 209-211 °C. ^{1}H NMR (600MHz, CDCl$_3$) δ(ppm): 8.50-8.48 (m, 4H), 7.96 (d, 2H, J = 16.8 Hz), 7.82 (d, 2H, J = 7.2 Hz), 7.48-7.46 (m, 4H), 7.31 (d, 4H, J = 16.8 Hz), 7.07 (t, 2H, J = 7.2 Hz), 6.97, (d, 2H, J = 8.4 Hz), 3.83 (d, 4H, J = 6.0 Hz), 2.14-2.09 (m, 2H), 1.02 (d, 12H, J = 8.4 Hz); ^{13}C NMR (150MHz, $CDCl_3$) δ (ppm): 156.95, 133.45, 133.07, 129.73, 129.07, 127.36, 125.98, 125.20, 120.73, 112.07, 74.90, 29.85, 28.65, 19.56. HRMS (ESI): calcd. for $C_{38}H_{38}O_2H$ 527.2945 $[M + H]^+$; found 527.2944. Purity: 98.65% (HPLC, t_R = 11.782 min).

2 References

1. W. Liu, et al. *Chem. Commun*., 2013, **49**, 6042
2. H. Zhang, et al. *Chem. Mater.* 2009, **21**, 5125.
3. C. Wang, et al. *Chem. Eur. J.* 2011, **17**, 3322.
4. X. Zhang, et al. *Chem. Commun.*, 2012, **48**, 10895

3 Figs. S1-S5



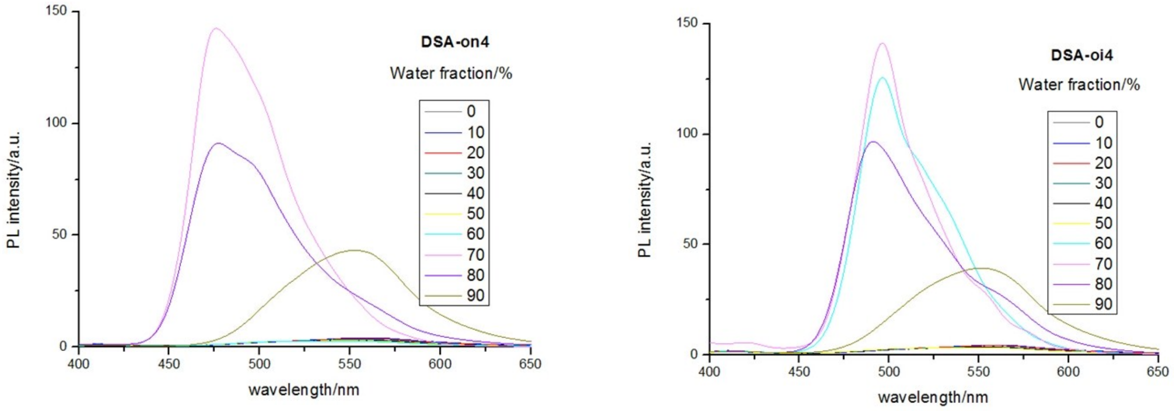
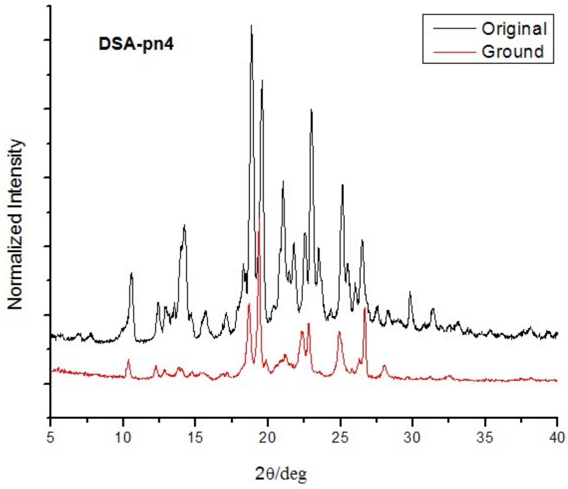
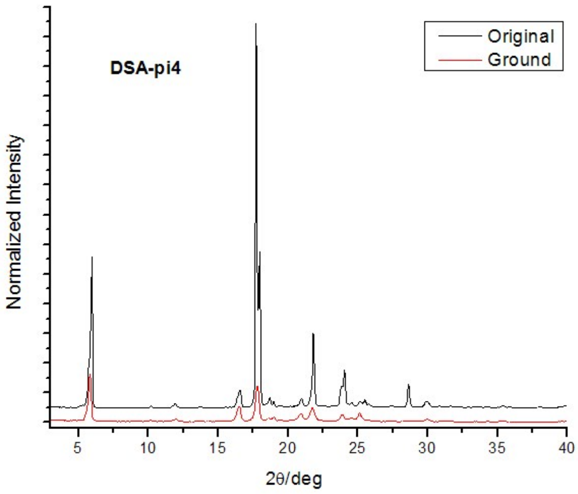
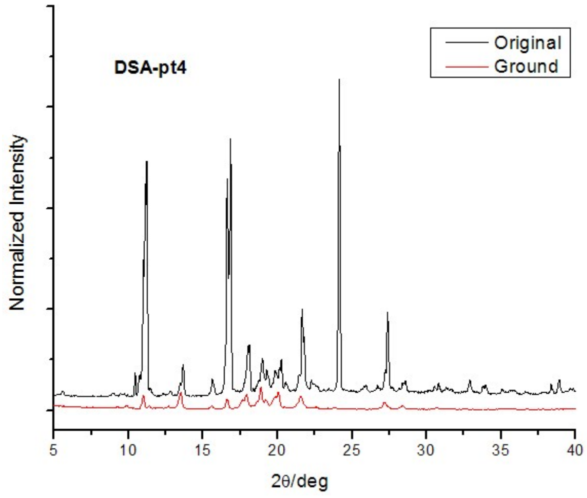


Fig S1 PL spectra of **DSA$_4$** in different concentrations of THF aqueous solutions







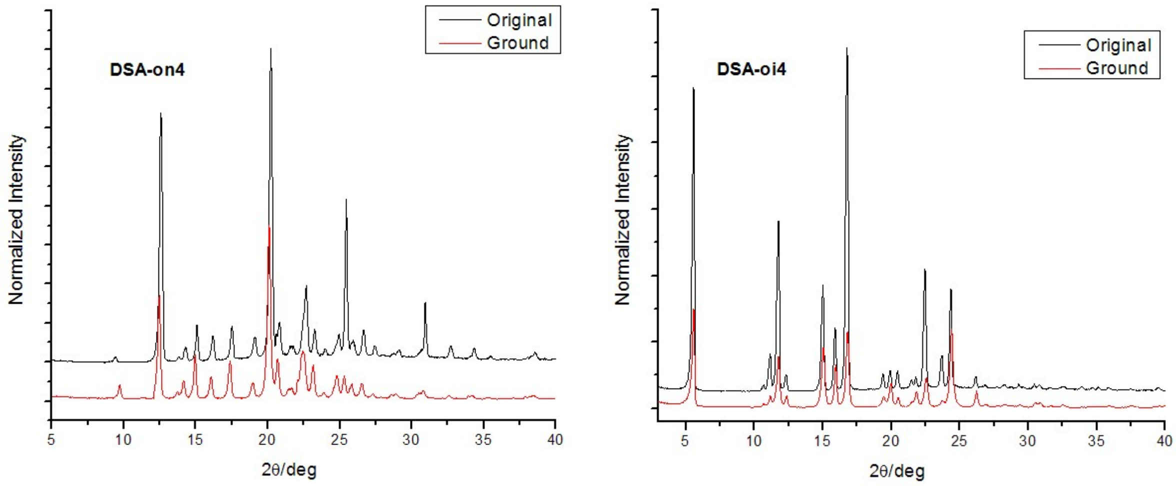


Fig. S2 Powder X-ray diffraction patterns of pristine and ground $\mathbf{DSA_4}$ at room temperature

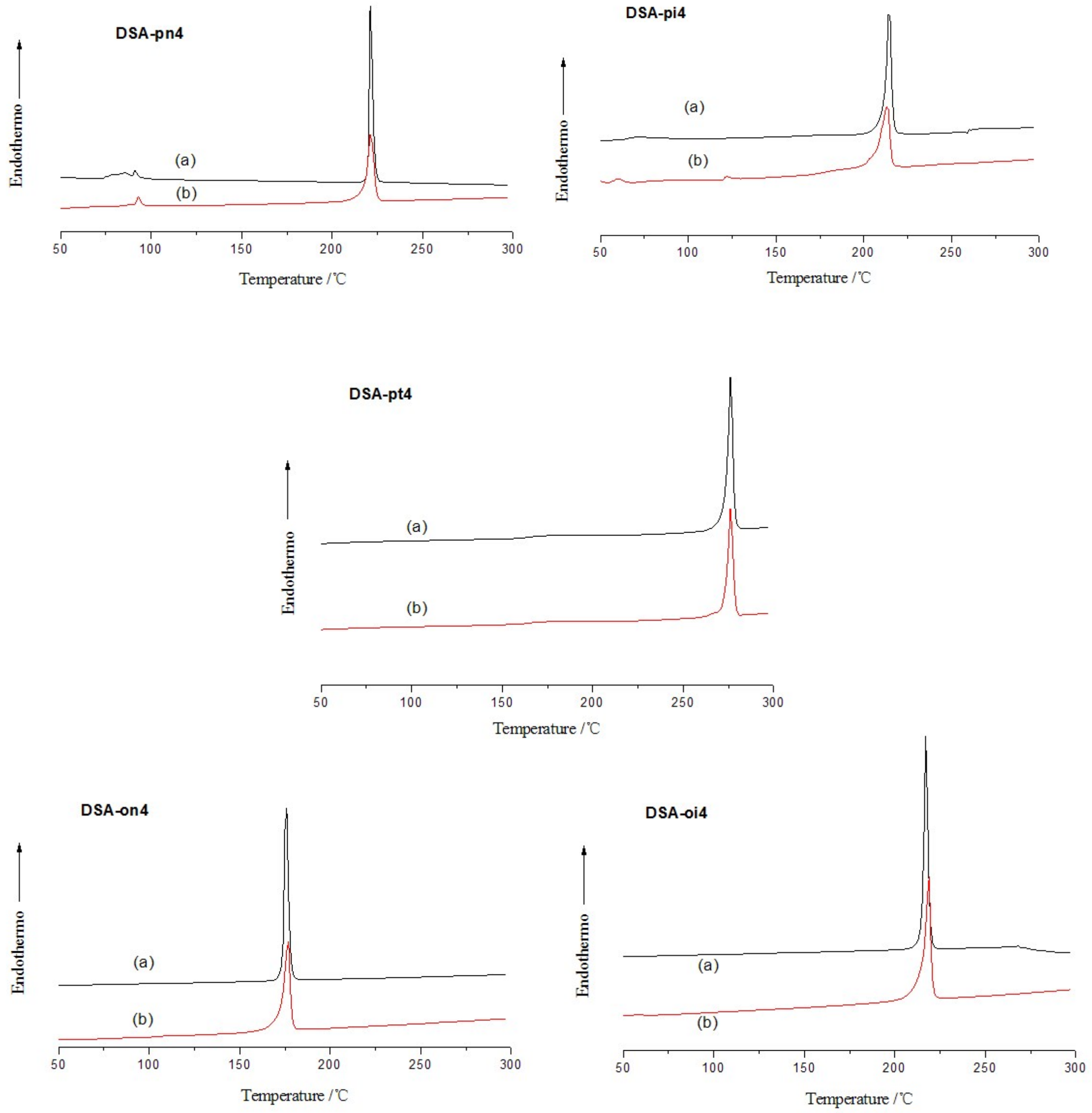


Fig. S3 DSC curves recorded for pristine and ground $\mathbf{DSA_4}$ solids (a) pressed sample;

(b) fumed sample

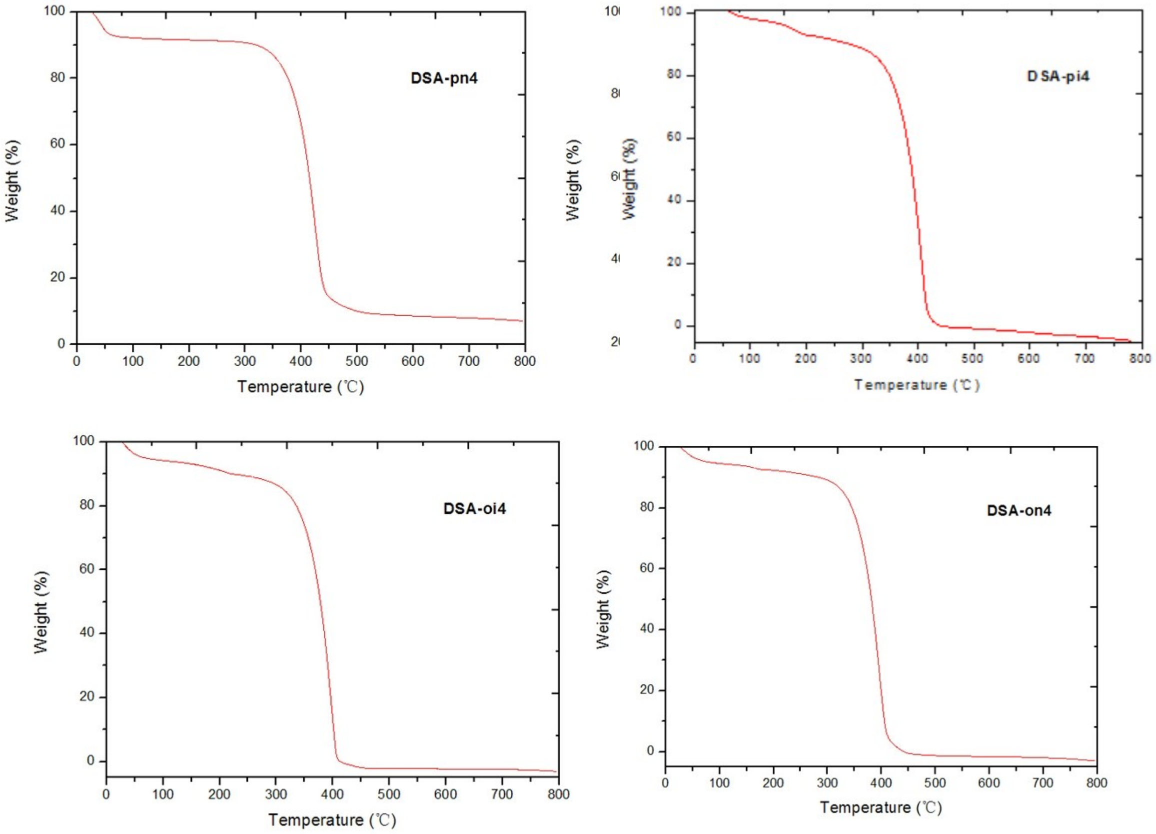
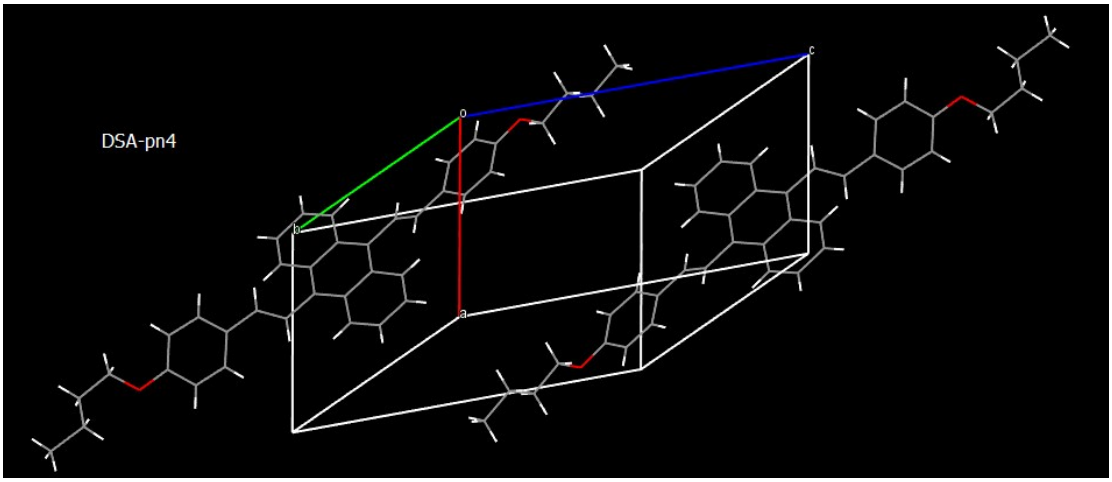
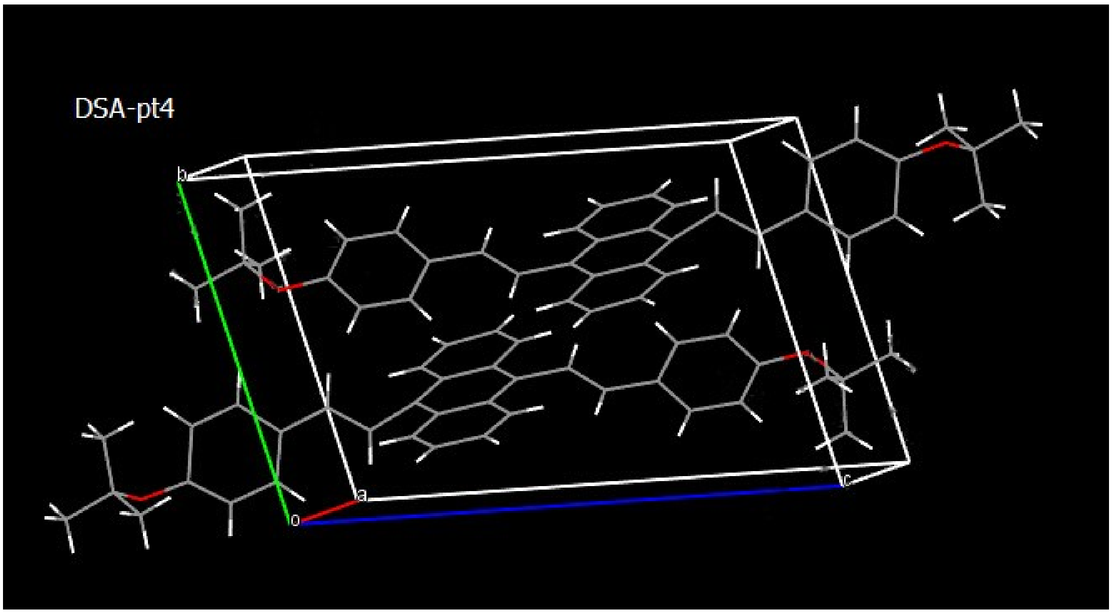


Fig. S4 TGA curves for isomers of $\mathbf{DSA_4}$





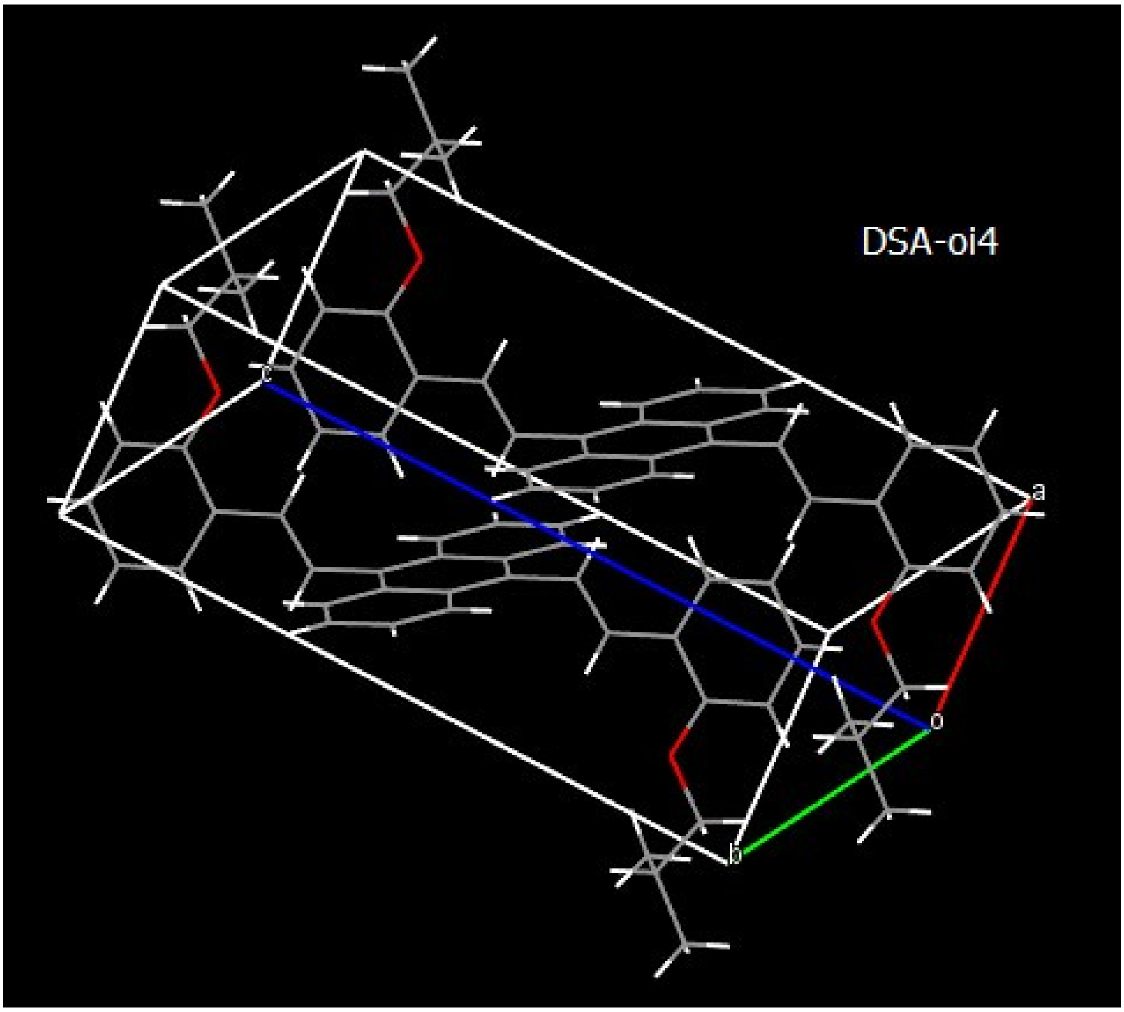


Fig. S5 Stacking modes of **DSA-pn4**, **DSA-pt4** and **DSA-oi4** molecules in crystals

4 ^{1}H NMR, ^{13}C NMR, HRMS spectra and HPLC

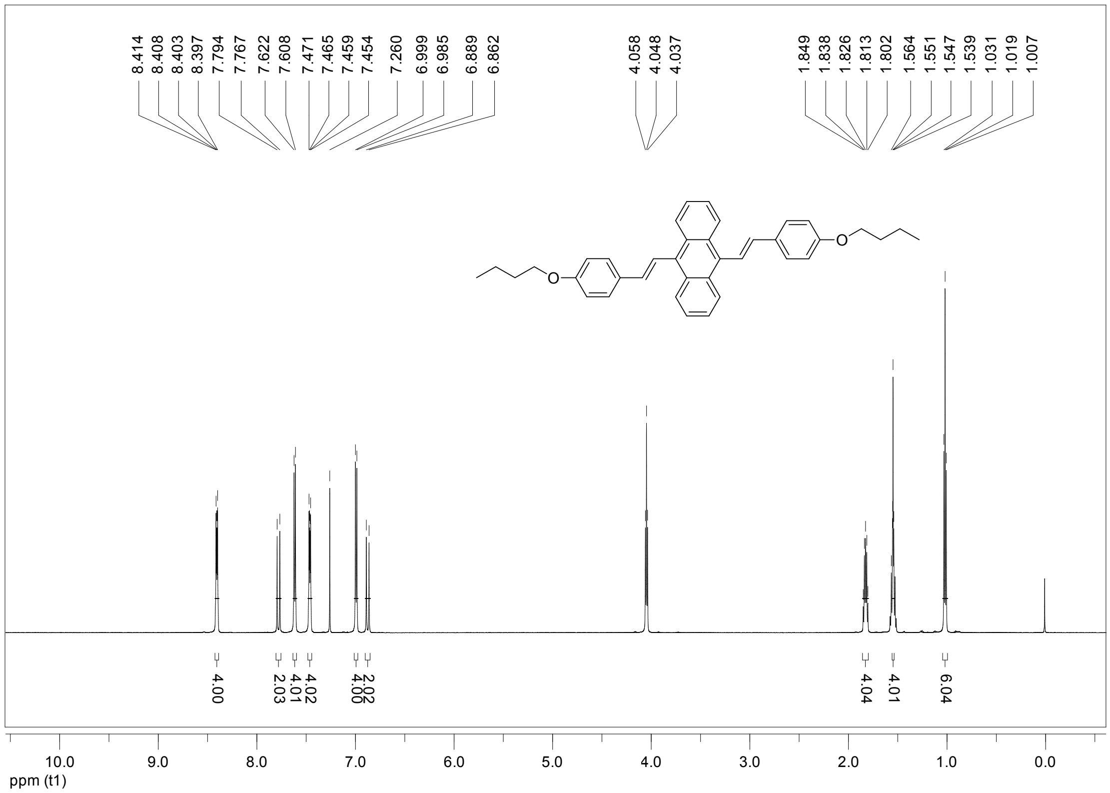


Fig. S6 ^{1}H NMR spectrum of **DSA-pn4**

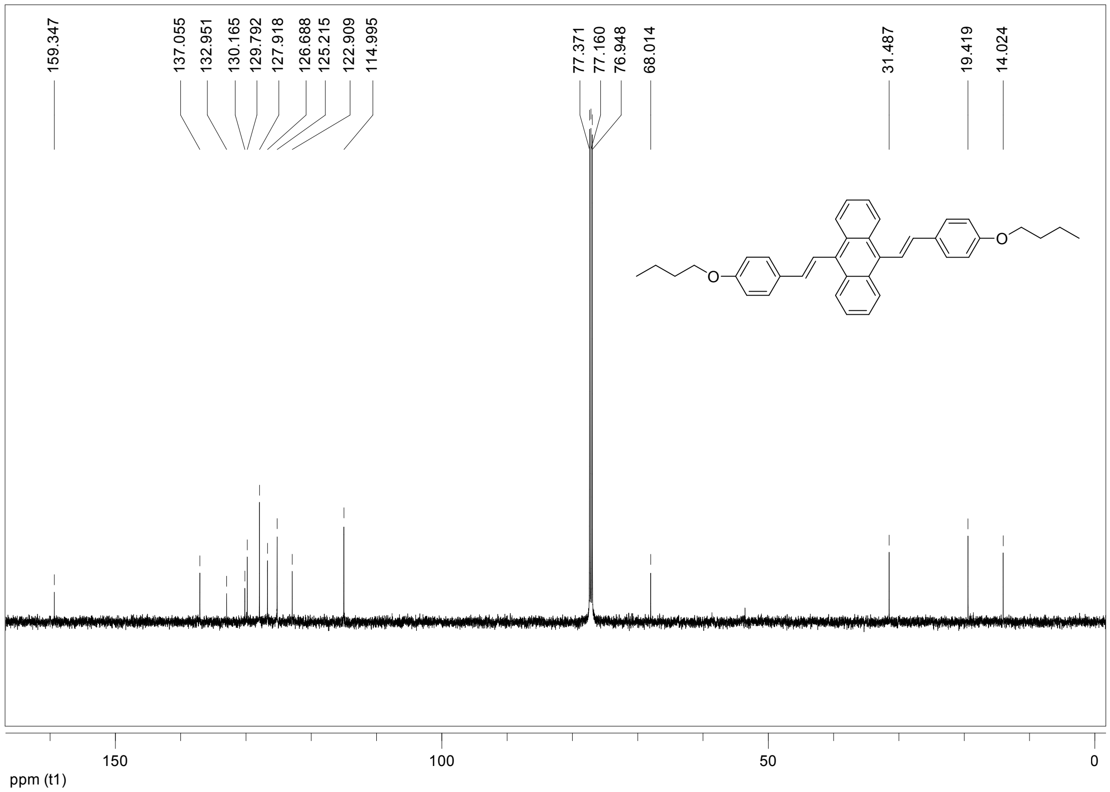


Fig. S7 ^{13}C NMR spectrum of **DSA-pn4**

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
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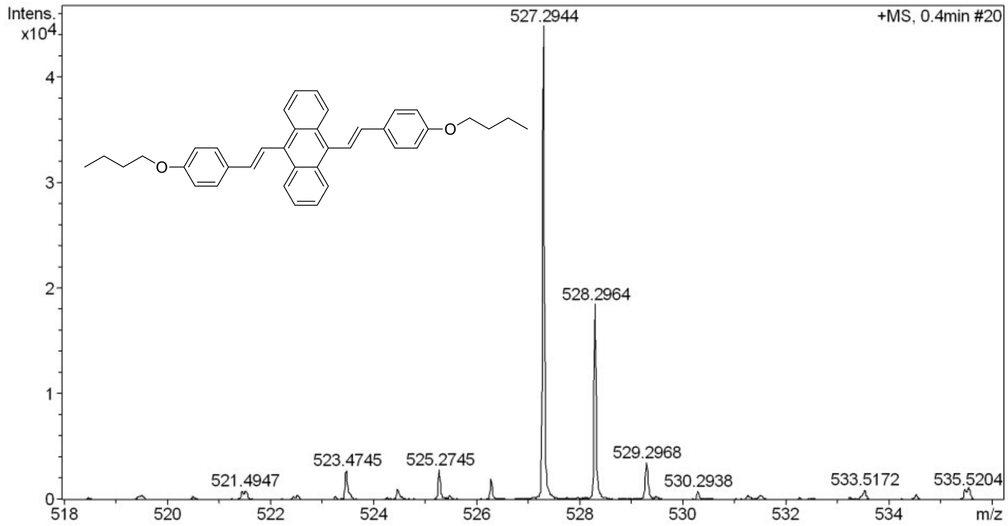
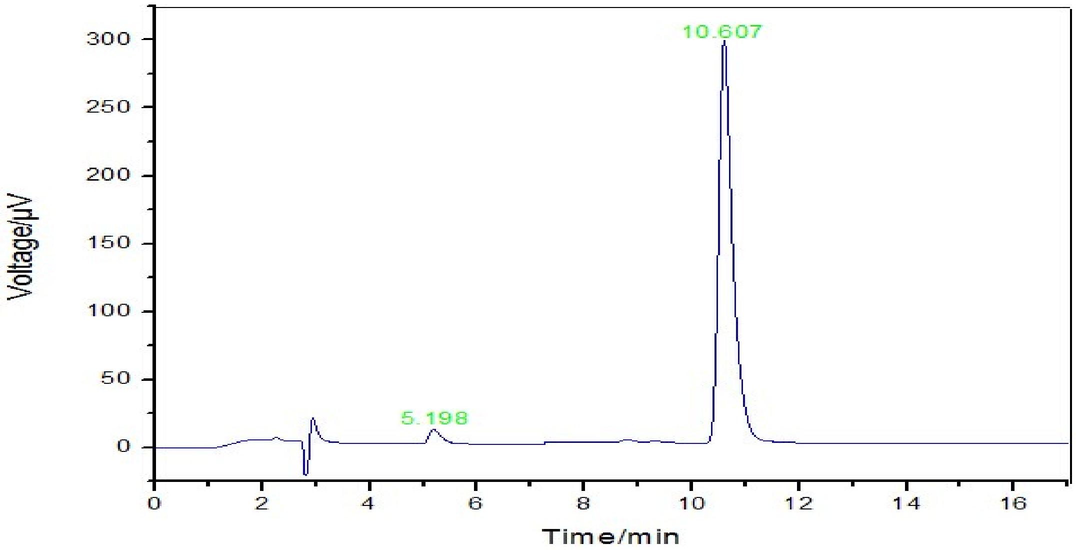


Fig. S8 HRMS spectrum of **DSA-pn4**



Peak		RT(min)	Height(μV)	Area(μV*min)	Area%
1		5.198	10.485	170825.857	3.05
2		10.607	295.756	5430554.000	96.95
Total			306.241	5601379.857	100.00

Fig. S9 HPLC spectrum of **DSA-pn4**

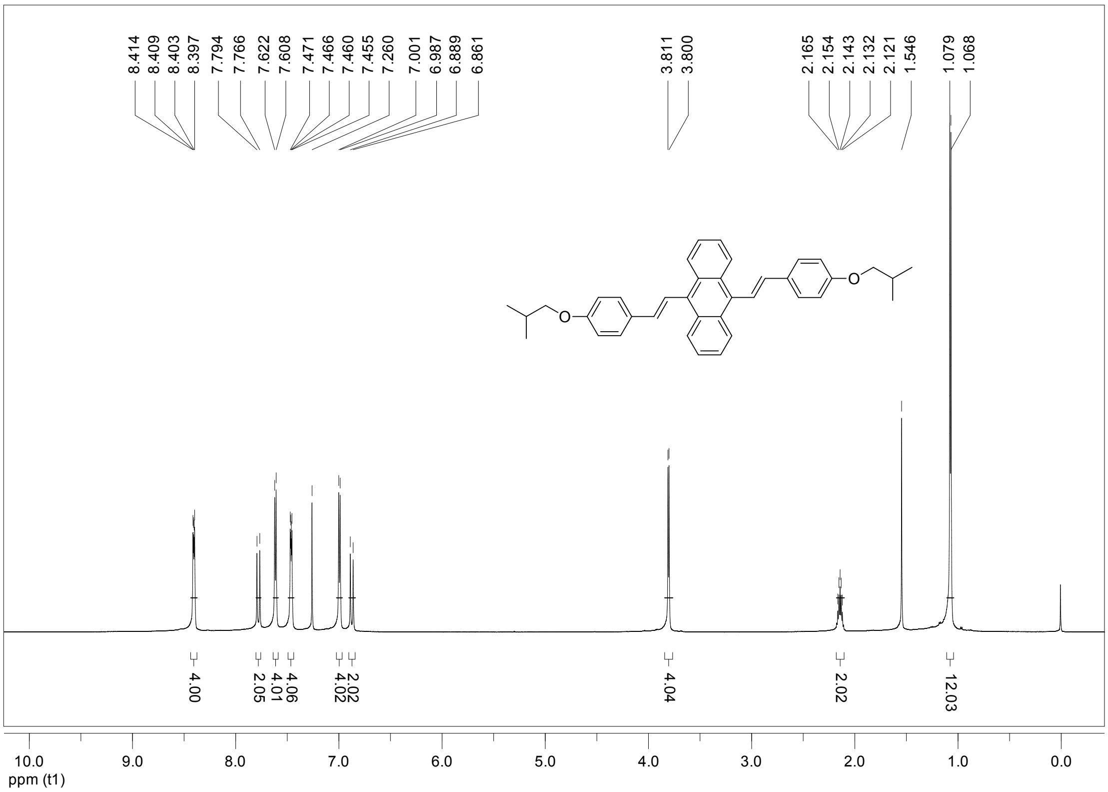


Fig. S10 ^{1}H NMR spectrum of **DSA-pi4**

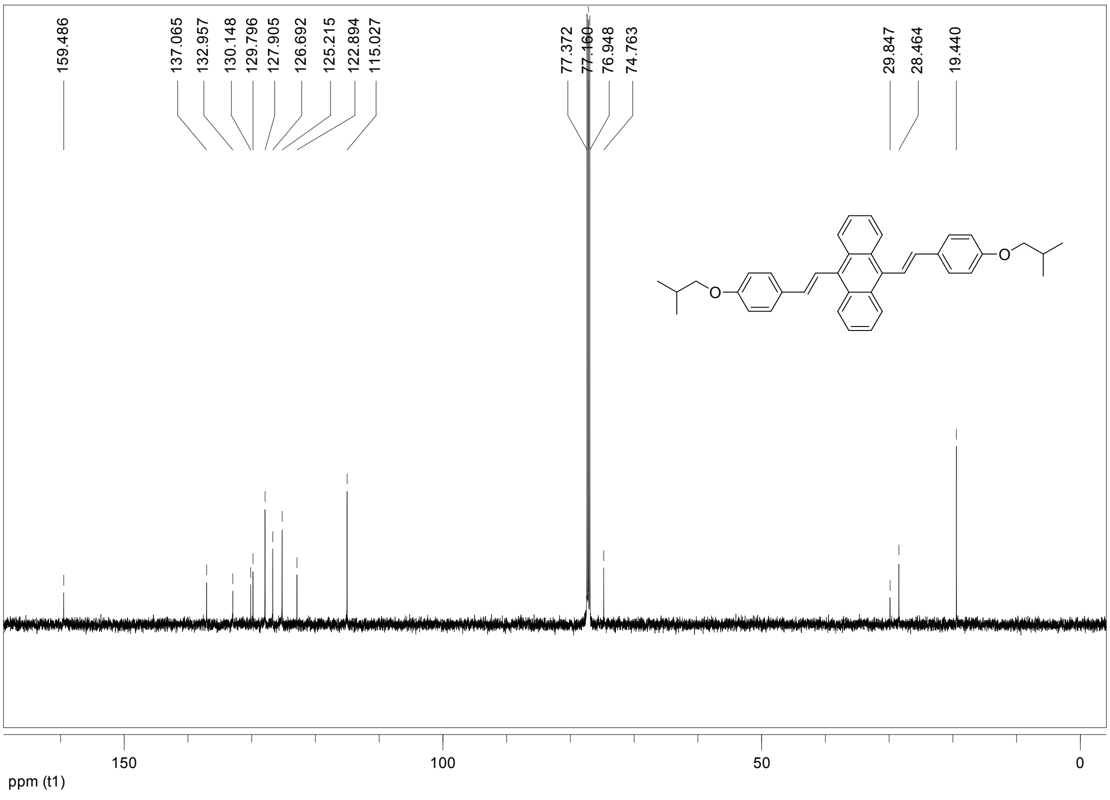


Fig. S11 ^{13}C NMR spectrum of **DSA-pi4**

Acquisition Parameter

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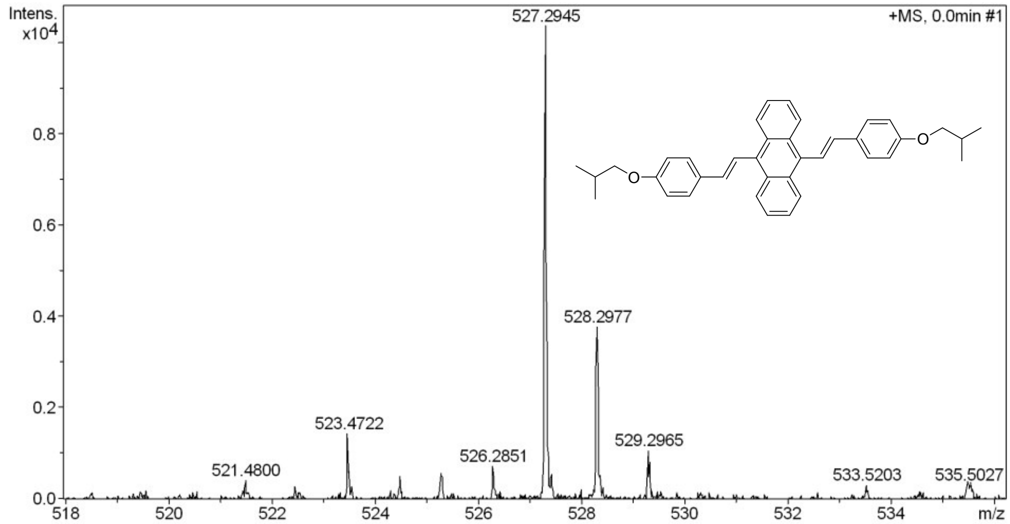
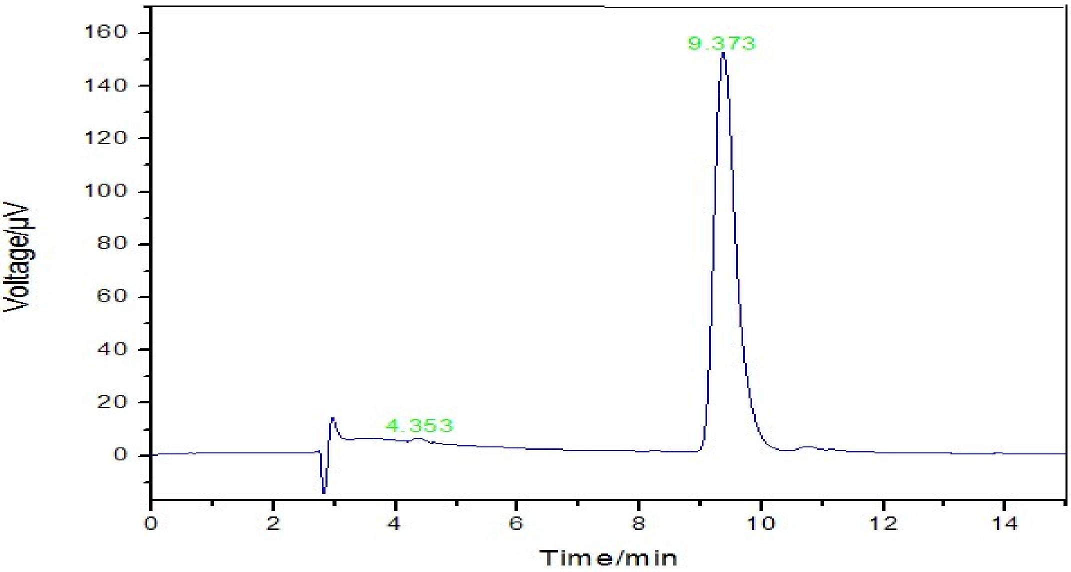


Fig. S12 HRMS spectrum of **DSA-pi4**



Peak		RT(min)	Height(μV)	Area(μV*min)	Area%
1		4.353	1.948	26848.172	0.70
2		9.373	295.756	3828112.000	99.30
Total			297.704	3854960.172	100.00

Fig. S13 HPLC spectrum of **DSA-pi4**

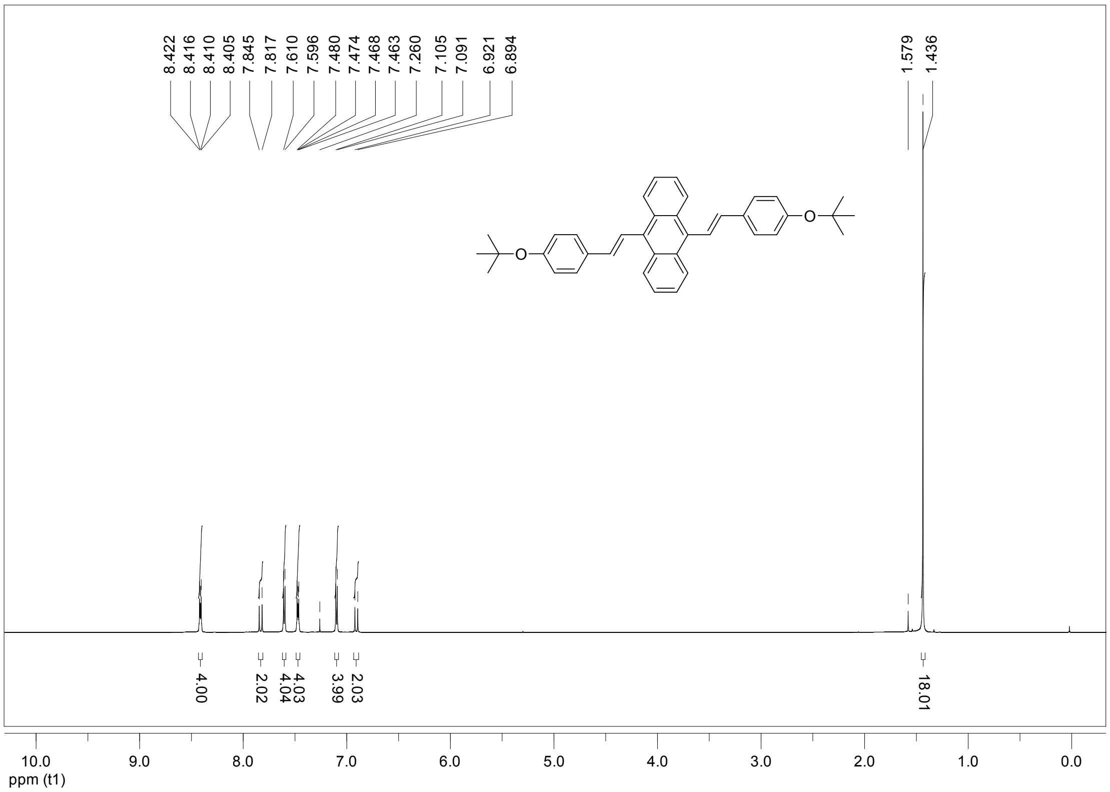


Fig. S14 ^{1}H NMR spectrum of **DSA-pt4**

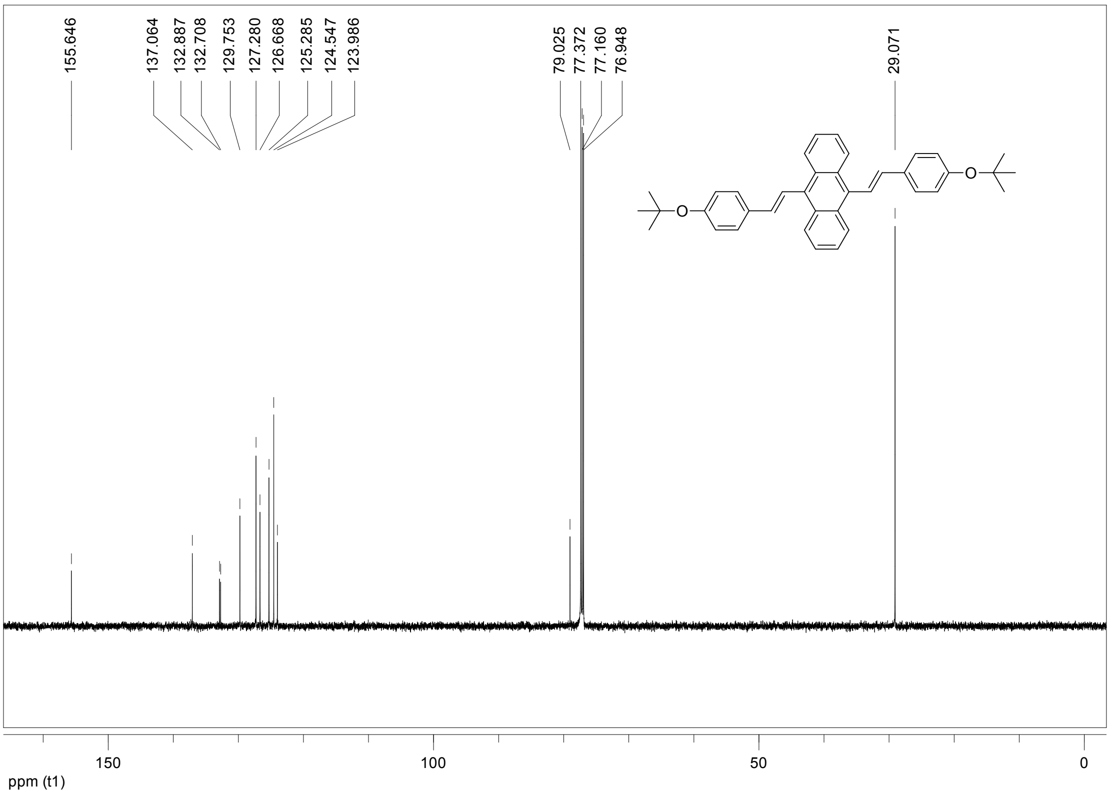


Fig. S15 ^{13}C NMR spectrum of **DSA-pt4**

Acquisition Parameter

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Scan End	2000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

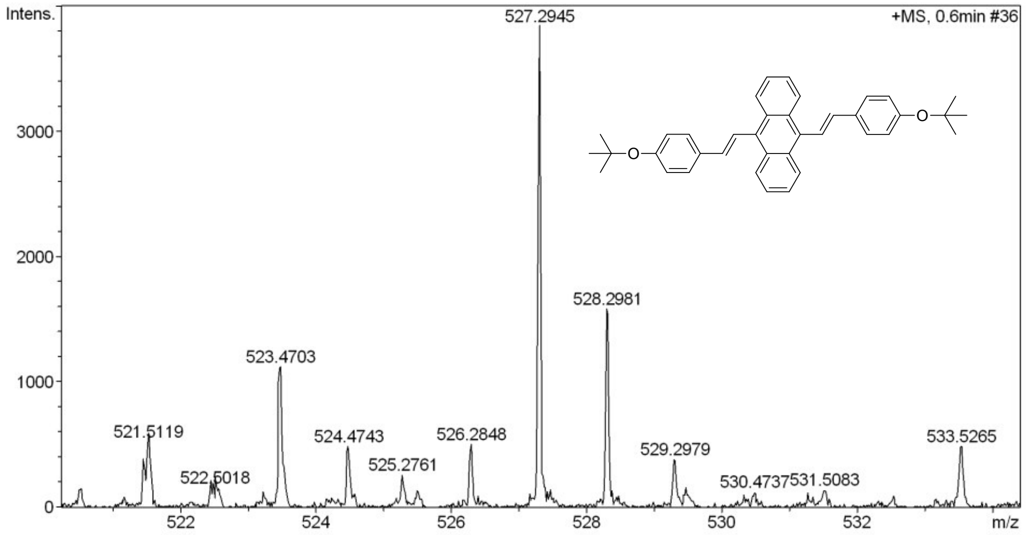
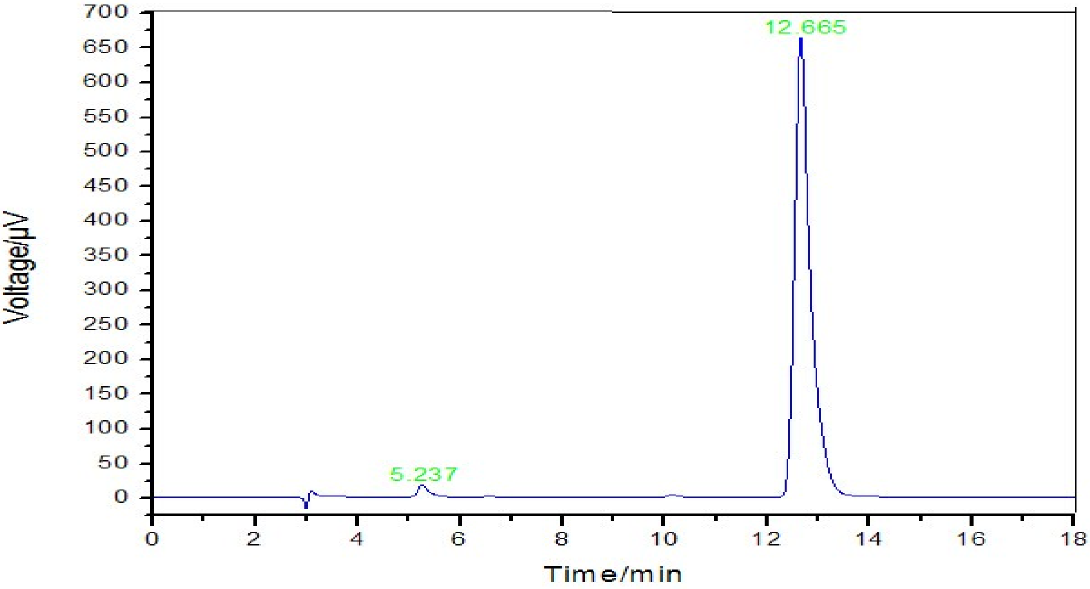


Fig. S16 HRMS spectrum of **DSA-pt4**



Peak		RT(min)	Height(μV)	Area(μV*min)	Area%
1		5.237	17.514	249799.281	1.67
2		12.665	664.107	14698786.000	98.33
Total			681.621	14948585.281	100.00

Fig. S17HPLC spectrum of **DSA-pt4**

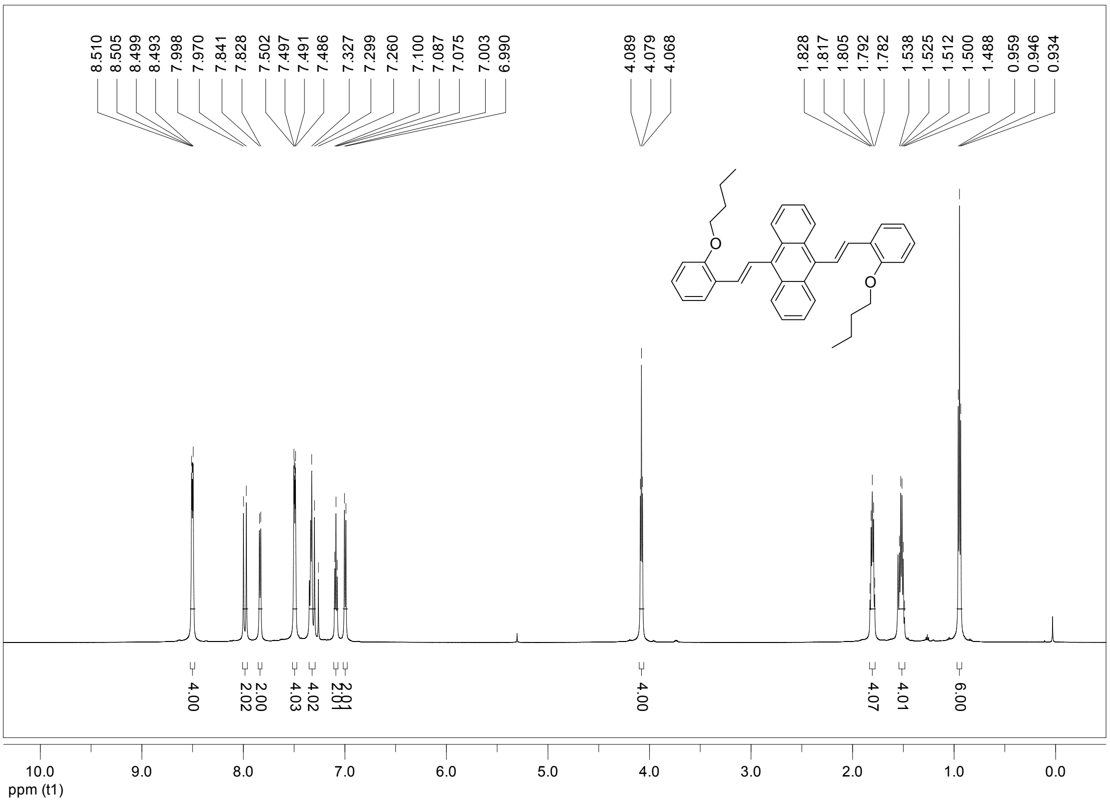


Fig. S18 ^{1}H NMR spectrum of **DSA-on4**

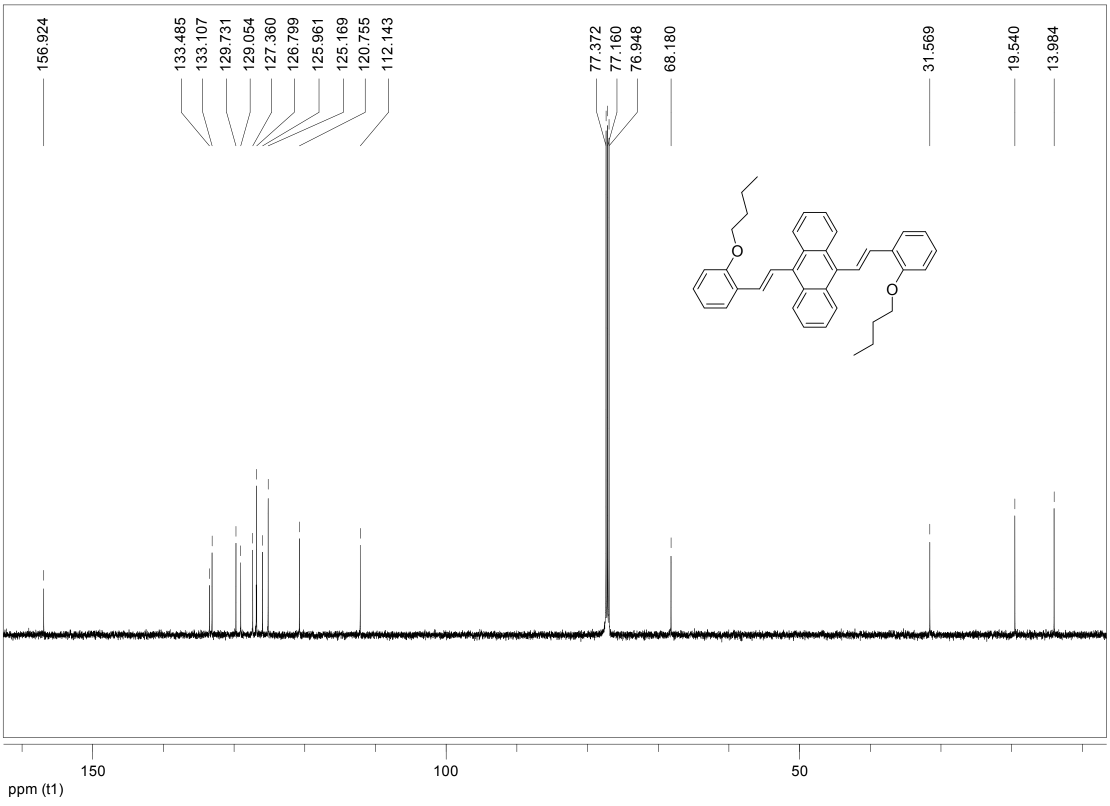


Fig. S19 ^{13}C NMR spectrum of **DSA-on4**

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Scan End	2000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

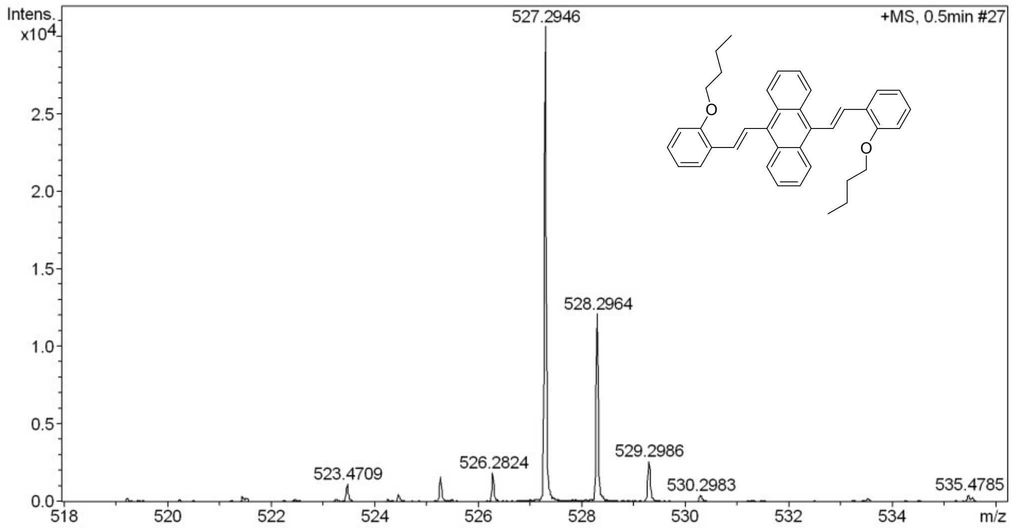
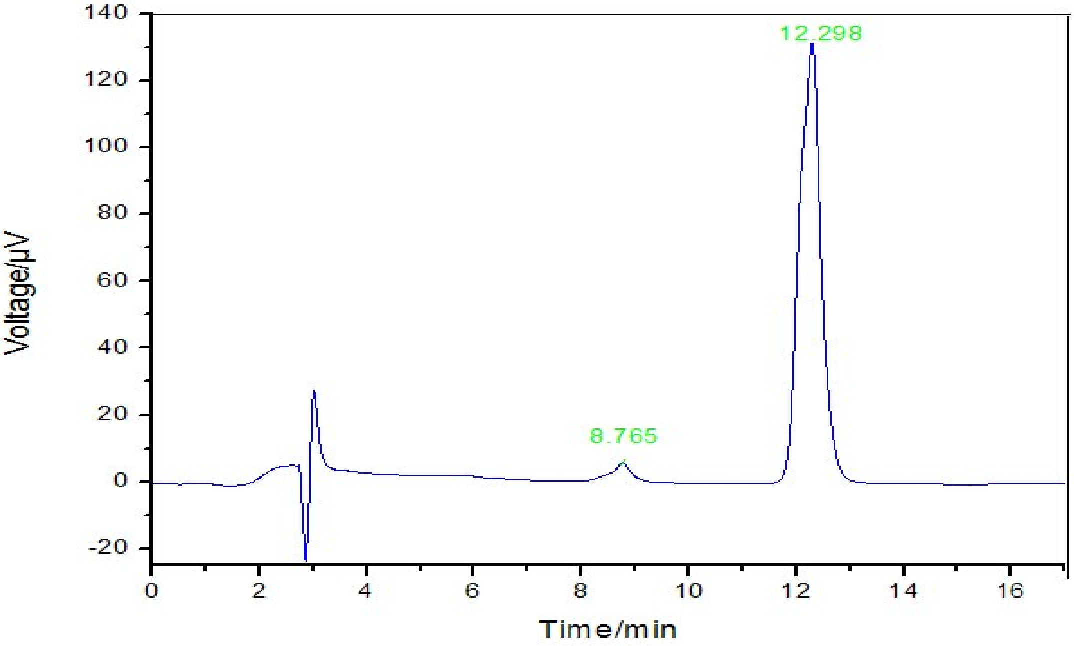


Fig. S20 HRMS spectrum of **DSA-on4**



Peak		RT(min)	Height(μV)	Area(μV*min)	Area%
1		8.765	5.647	156183.000	2.60
2		12.298	131.949	3777799.500	97.40
Total			137.596	3933982.500	100.00

Fig. S21 HPLC spectrum of **DSA-on4**

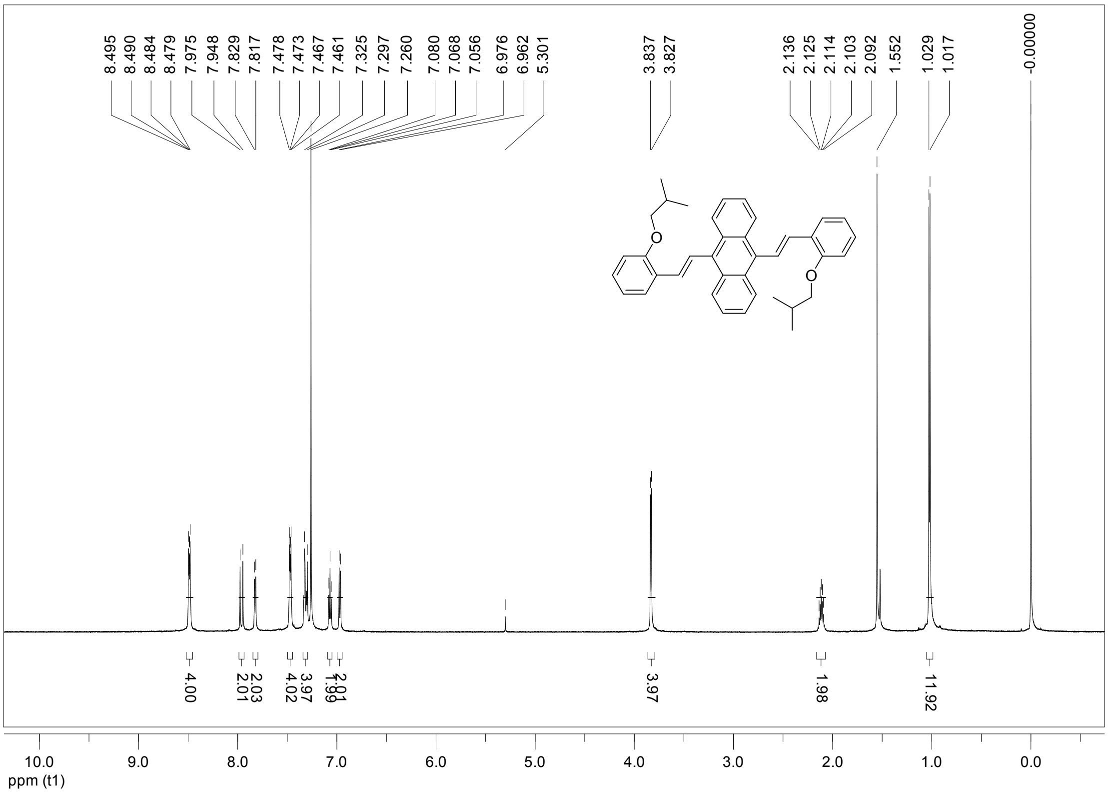


Fig. S22 ^{1}H NMR spectrum of **DSA-oi4**

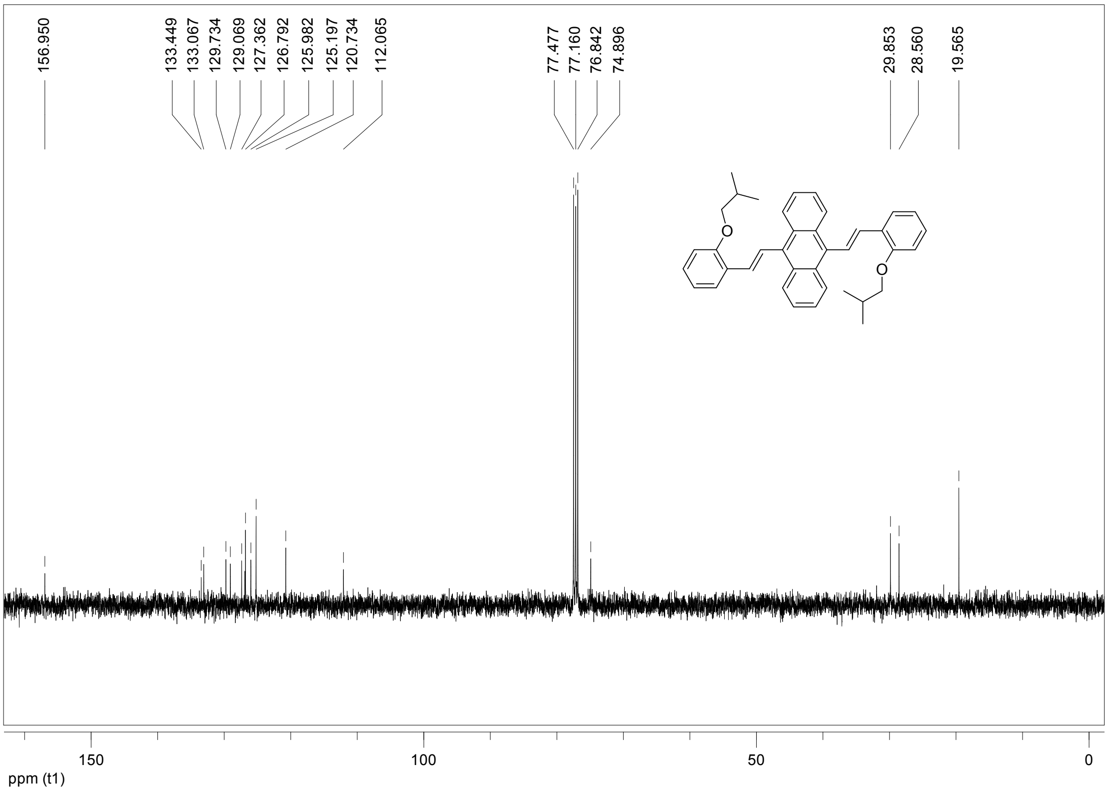
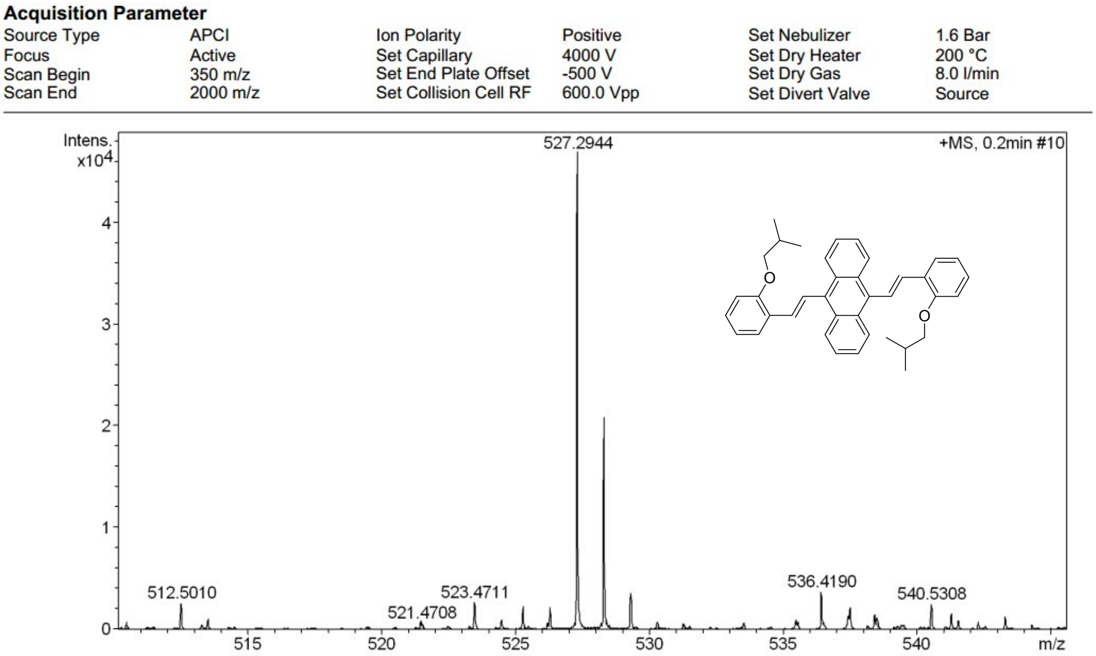


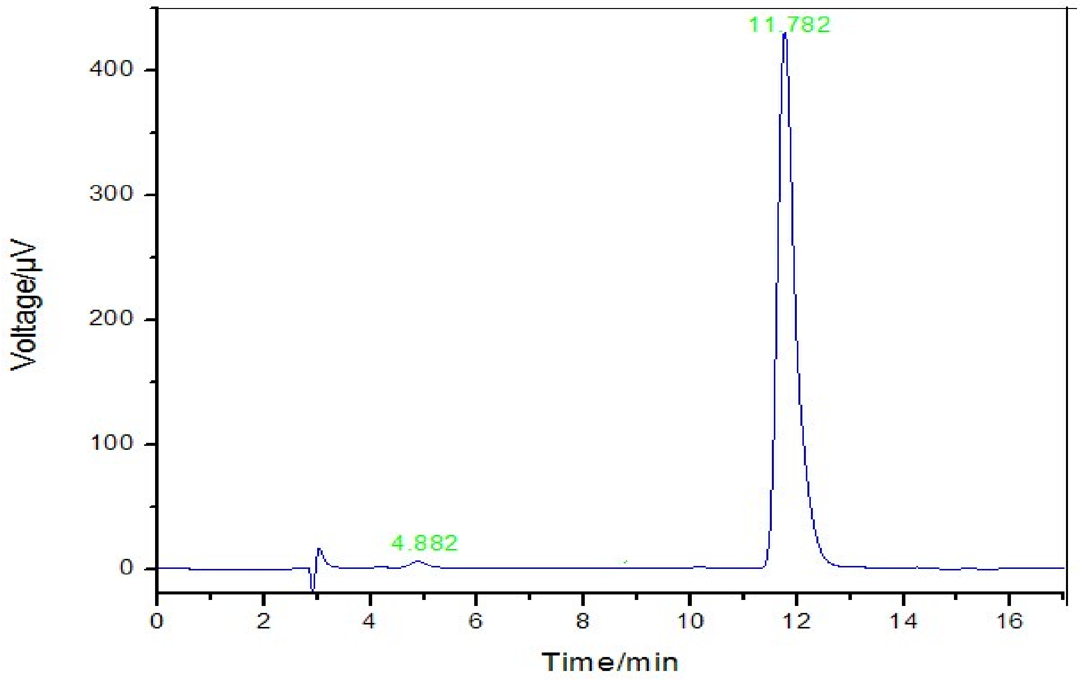
Fig. S23 ^{13}C NMR spectrum of **DSA-oi4**



Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	350 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

Fig. S24 HRMS spectrum of **DSA-oi4**



Peak		RT(min)	Height(μV)	Area(μV*Sec)	Area%
1		4.882	5.922	164561.063	1.35
2		11.782	430.687	10530369.000	98.65
Total			436.609	10694930.063	100.00

Fig. S25 HPLC spectrum of **DSA-oi4**

5 Crystallographic data

Table S1 Crystallographic data of **DSA-pn4**

Empirical formula	C_{38} H_{38} O_2
Formula weight	526.68
Temperature	292.1(4) K
Wavelength	0.7107 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.6115(5) Å alpha = 110.013(6) deg.
	b = 12.5777(8) Å beta = 107.490(5) deg.
	c = 14.3804(10) A gamma = 99.474(5) deg.
Volume	1486.96(15) Å^3
Z, Calculated density	2, 1.150 Mg/m^3
Absorption coefficient	0.069 mm^{-1}
F (000)	552
Crystal size	0.3900 x 0.2100 x 0.0700 mm
Theta range for data collection	3.00 to 26.37 deg.
Limiting indices	-11<=h<=12, -15<=k<=15, -17<=l<=17
Reflections collected / unique	12303 / 6064 [R (int) = 0.0251]
Completeness to theta = 26.37	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.64979
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6064 / 5 / 364
Goodness-of-fit on F^2	1.040
Final R indices [I>2 sigma (I)]	R_1 = 0.0674, wR^2 = 0.1743
R indices (all data)	R_1 = 0.1051, wR^2 = 0.2033
Extinction coefficient	0.014(2)
Largest diff. peak and hole	0.429 and -0.311 e. A^{-3}

Table S2 Crystallographic data of **DSA-pt4**

Empirical formula	C_{38} H_{38} O_2
Formula weight	526.68
Temperature	100.00(10) K
Wavelength	1.54184 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.3559(4) Å alpha = 99.935(3) deg.
	b = 9.9674(3) Å beta = 101.993(4) deg.
	c = 16.4761(8) Å gamma = 96.700(3) deg.
Volume	1461.72(10) Å^3
Z, Calculated density	2, 1.197 Mg/m^3
Absorption coefficient	0.554 mm^{-1}

F (000)	564
Crystal size	0.3400 x 0.1600 x 0.0300 mm
Theta range for data collection	4.56 to 67.07 deg.
Limiting indices	-10<=h<=11, -11<=k<=7, -19<=l<=19
Reflections collected / unique	9459 / 5219 [R (int) = 0.0168]
Completeness to theta = 67.07	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.69813
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5219 / 0 / 419
Goodness-of-fit on F^2	1.056
Final R indices [I>2 sigma (I)]	$R_1 = 0.0409$, $wR^2 = 0.1098$
R indices (all data)	$R_1 = 0.0447$, $wR^2 = 0.1139$
Largest diff. peak and hole	0.203 and -0.246 e. A^{-3}

Table S3 Crystallographic data of **DSA-oi4**

Empirical formula	$C_{38} H_{38} O_2$
Formula weight	526.68
Temperature	293.20(10) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 5.5707(5) Å alpha = 92.864(8) deg.
	b = 8.2832(9) Å beta = 96.899(7) deg.
	c = 15.9643(15) Å gamma = 93.150(8) deg.
Volume	729.02(12) $Å^3$
Z, Calculated density	1, 1.200 Mg/m^3
Absorption coefficient	0.072 mm^{-1}
F (000)	282
Crystal size	0.43 x 0.07 x 0.02 mm
Theta range for data collection	3.46 to 26.37 deg.
Limiting indices	-6<=h<=6, -10<=k<=10, -19<=l<=19
Reflections collected / unique	8992 / 2948 [R (int) = 0.0518]
Completeness to theta = 26.37	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.51927
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2948 / 0 / 184
Goodness-of-fit on F^2	1.076
Final R indices [I>2 sigma (I)]	$R_1 = 0.0574$, $wR^2 = 0.1558$
R indices (all data)	$R_1 = 0.0788$, $wR^2 = 0.1760$
Extinction coefficient	0.025(6)
Largest diff. peak and hole	0.255 and -0.151 e. A^{-3}